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TI Lead-free solder of tin-aluminum-indium-silver alloy for low temperature use

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SO Jpn. Kokai Tokkyo Koho, 5 pp.)

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AB	The solder of Sn alloy contains Al 0.01-3.0, In 0.1-5.0, Ag 0.1-6.0, Cu 0-6.0, and Zn 0-10.0%.				

Oxide materials, e.g., glasses, ceramics, can be strongly bonded with the solder.

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 11-054716

(71)Applicant : NIPPON SHEET GLASS CO LTD

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(30)Priority

Priority number : 10253852 Priority date : 08.09.1998 Priority country : JP

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(54) LEADLESS SOLDER

(57)Abstract:

PROBLEM TO BE SOLVED: To improve joining strength to oxide materials such as glass and ceramics by composing solder of specified compositions of Al, In, Ag, Cu, and Zn and the balance Sn.

SOLUTION: A solder is composed, by weight, of 0.01-3.0% Al, 0.1-50% In, 0.1-6.0% Ag, 0-6.0% Cu, 0-10.0% Zn and the balance Sn. Sn has no toxicity and is an indispensable composition to execute wetting of an object to be joined. Al is liable to form combination in a joining with oxide. In improves wettability and softens solder itself as well as decreases melting point of solder. Ag and Cu improve mechanical strength of solder. Zn imparts adhesive strength to oxide materials such as glass and ceramics. Solder is further preferably to be added with  $\leq 10$  wt.% of  $\geq$  one kind among Sb, Ti, Si and Bi.

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## CLAIMS

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[Claim(s)]

[Claim 1] The unleaded pewter with which it displays by weight % and 0.01 - 3.0% of aluminum, 0.1 - 50% of In, 0.1 - 6.0% of Ag, 0 - 6.0% of Cu, 0 - 10.0% of Zn, and the remainder are characterized by the bird clapper from Sn.

[Claim 2] The unleaded pewter according to claim 1 which displays by weight % and contains 0.01 - 1.0% of aluminum.

[Claim 3] The unleaded pewter according to claim 1 or 2 which displays by weight % and contains 0.1 - 30% of In.

[Claim 4] The unleaded pewter according to claim 1 to 3 which displays by weight % and contains 0.1 - 3.5% of Ag.

[Claim 5] The unleaded pewter according to claim 1 to 4 which displays by weight % and contains 0.1 - 1.0% of Cu with percentage by weight.

[Claim 6] The unleaded pewter according to claim 1 to 5 which displays by weight % and contains 0.01 - 7.0% of Zn.

[Claim 7] The unleaded pewter according to claim 1 to 6 which contains one or more kinds of elements which display by weight % and are chosen from among Sb, Ti, Si, or Bi in a total of 10% or less of range.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the unleaded pewter for oxide material junction of the ceramics which can work at low temperature, glass, etc.

[0002]

[Description of the Prior Art] Although the method of performing electroplating and electroless deposition, such as gold plate, copper coating, and nickel plating, beforehand for soldering of oxide material, such as ceramics and glass, is common knowledge conventionally, to solder at an expensive price [ soldering to a plating side ], intricately, and more economically is demanded.

[0003] It is indicated by glass and ceramics about the Pb-Sn system pewter which can carry out direct soldering at JP,49-22299,B or JP,52-21980,B to meet this request.

[0004] However, lead is a strong toxic metal, we are anxious about the influence of the health and environment on leaden, the bad influence to an ecosystem and contamination are being regarded as questionable, and the movement which makes a pewter unleaded is spreading quickly in recent years.

[0005]

[Problem(s) to be Solved by the Invention] Although the pewter currently indicated by above-mentioned JP,49-22299,B is a Pb-Sn-Cd-Sb pewter in which direct soldering to oxide film material, such as glass and ceramics, is possible, since this pewter contains the lead of a toxic substance, if the waste of the product using these pewters is exposed to acid rain, lead will be eluted in large quantities and the toxicity will pose a very serious problem.

[0006] Moreover, although the pewter indicated by above-mentioned JP,52-21980,B is a rare earth-metal content pewter usable to junction of oxide material, such as glass and ceramics, a principal component is lead and this pewter also has the same problem.

[0007] On the other hand, as a unleaded pewter, research is mainly briskly made as an object for electronic-parts mounting. For example, although it is indicated by JP,9-326554,A about the Sn-Ag-In pewter and indicated by JP,8-164495,A about the Sn-Zn-Bi pewter, all have the trouble that the bonding strength of a pewter is not enough, in soldering to oxide material, such as glass and ceramics.

[0008] Furthermore, although indicated by JP,55-36032,B about the Sn-Ag-aluminum-Zn pewter to the metallic oxide as a unleaded pewter which can be soldered, since the metal is chosen as a transconjugant, when it is used to oxide material which a coefficient of thermal expansion is large and is different, such as glass and ceramics, it has the trouble of being easy-to-exfoliate.

[0009] this invention is made in view of the above-mentioned conventional actual condition, and it aims at offering the unleaded pewter which has sufficient bonding strength to oxide material, such as glass and ceramics, excluding the lead of a toxic substance.

[0010]

[Means for Solving the Problem] this invention is made in order to join oxides, such as glass and ceramics, and it is considered as the composition which contains aluminum, In, Ag, Cu, and Zn in the pewter which makes Sn a principal component.

[0011] That is, the unleaded pewter of this invention is displayed by weight %, and 0.01 - 3.0% of aluminum, 0.1 - 50% of In, 0.1 - 6.0% of Ag, 0 - 6.0% of Cu, 0 - 10.0% of Zn, and the remainder are characterized by the

bird clapper from Sn.

[0012] Here, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.01 - 1.0% of aluminum.

[0013] Moreover, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.1 - 30% of In.

[0014] Furthermore, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.1 - 3.5% of Ag.

[0015] Furthermore, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.1 - 1.0% of Cu.

[0016] Furthermore, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.01 - 7.0% of Zn.

[0017] Moreover, as for the unleaded pewter of this invention, it is desirable to contain one or more kinds of elements chosen from among Sb, Ti, Si, or Bi in a total of 10% or less of range.

[0018] Below, the reason for composition limitation of the unleaded pewter of this invention is explained.

However, the following composition is displayed by weight %.

[0019] Since Sn has operation of there being no toxicity and obtaining wetting to a transconjugant, it is a component indispensable to a pewter.

[0020] Although aluminum is an element which is very easy to oxidize, it has the advantage of being easy to build combination in junction to an oxide. At less than 0.01%, the effect has low aluminum addition, when it exceeds 3.0%, while it is difficult for own hardness of a pewter to secure increase and thermo-cycle-proof nature, the melting point is high, and workability gets worse. A more desirable addition is 0.01 - 1.0% of range.

[0021] It raises wettability and it not only reduces the melting point of a pewter, but it has operation of making the pewter itself soft. If In addition is low and the effect exceeds 50% at less than 0.1%, it will become a pewter's own on-the-strength securing not only becoming difficult but quite [ in cost ] expensive conversely. The range of a more desirable addition is 0.1 - 30%.

[0022] Ag demonstrates the effect excellent in improvement in the mechanical strength of a pewter by adding. At less than 0.1%, the effect has low Ag addition, improvement in a mechanical strength is not obtained, but if it exceeds 6.0%, while the melting point will become high, an intermetallic compound with Sn occurs so much, and that a mechanical strength falls conversely poses a problem. The range of a more desirable addition is 0.1 - 3.5%.

[0023] Cu demonstrates the effect which was excellent in improvement in the mechanical strength of a pewter by adding like above-mentioned Ag. If Cu addition exceeds 6.0%, while the melting point will become high like Ag, an intermetallic compound with Sn occurs so much, and that a mechanical strength falls conversely poses a problem. The range of a more desirable addition is 0.1 - 1.0%.

[0024] Zn is added by the pewter in order to give the adhesive strength to oxide material, such as glass and ceramics. If Zn addition exceeds 10.0%, the inclination for a pewter to become weak becomes remarkable and it is not desirable practically. The range of a more desirable addition is 0.01 - 7.0%, and the still more desirable range is 0.5 - 5.0%.

[0025] In the unleaded pewter of this invention, one or more kinds of elements can be suitably added in 10% or less of range among Sb, Ti, Si, or Bi. Sb makes soldering appearance good and increases creep resistance. Ti, Si, and Bi can make the wettability of a pewter improve. moreover -- in addition -- even if it carries out minute amount addition of the elements, such as Fe, nickel, Co, Ga, germanium, and P, -- the property as a pewter -- that is, it is unleaded and also soldering nature and a mechanical strength are raised -- things can be carried out

[0026] In addition, the unleaded pewter of this invention can be soldered direct to the difficulty soldering metal which has oxide skins, such as aluminum besides oxide material, such as glass and ceramics, titanium, and a zirconium. Moreover, when soldering to difficulty soldering material, it is desirable to use the equipment which can add supersonic oscillation to a pewter in the case of soldering.

[0027]

[Embodiments of the Invention] Hereafter, a concrete example is given and the operation gestalt of this invention is explained.

[0028] (Examples 1-14) Dissolution adhesion of the unleaded pewter which consists of composition shown in

Tables 1 and 2 was carried out on the frequency of 60kHz on the sheet glass using the ultrasonic soldering iron with which the trowel point vibrates, using a soda lime glass (50x50x3mm) as jointed material, and the sample of this example was created. Each composition of front Naka is a weight % display.

[0029] The ablation degree of the unleaded pewter at the time of deleting with a knife the unleaded pewter layer pasted up on the sheet glass front face performed adhesive evaluation of sheet glass and a unleaded pewter. As for the thing and x mark with which O mark remained on sheet glass in the adhesive column in Table 1 and 2, without more than the half of a pewter layer exfoliating, all pewter layers exfoliate.

[0030]

[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10
S n	62.2	63.95	45.5	88	85	70.5	50	67	76	65
A l	0.5	0.05	2.5	0.5	0.5	1	2.5	0.5	0.5	1
I n	30	28	40	1	10	26	45	30	15	28
A g	2.3	2.5	2.5	3.5	3	2	1.5	0.5	6	2.3
C u	0	0	0	0	0	0	0	0	0.5	0.7
Z n	5	5.5	9.5	7	1.5	0.5	1	2	2	3
合計	100	100	100	100	100	100	100	100	100	100
接着性	○	○	○	○	○	○	○	○	○	○

[0031]

[Table 2]

	実施例11	実施例12	実施例13	実施例14	比較例1	比較例2	比較例3
S n	65	69	64	68	77.2	70	96.5
A l	0.5	0.5	1	0.95	0	0	0
I n	26	26	28	28.4	20	0	0
A g	2.5	0.5	2	2.5	2.8	0	3.5
C u	5	3	2	0.05	0	1	0
Z n	1	1	3	0.1	0	29	0
合計	100	100	100	100	100	100	100
接着性	○	○	○	○	×	×	×

[0032] So that clearly from Tables 1 and 2 the sample of this example By making components, such as aluminum, In, Zn, Ag, and Cu, contain appropriately, as shown in a claim 1 Since it not only increases a bond strength with glass, but has various properties required in order to paste up firmly pewters, such as own mechanical strength of a pewter and distortion relief of the glass-pewter interface at the time of cooling, and glass, Glass can be firmly joined with a pewter and the problem of ablation by the shock after soldering etc. is not produced at all.

[0033] (The example 1 of comparison, or 3) The composition and the adhesive property of the example of comparison over this invention are shown in Table 2. Composition is a weight % display.

[0034] the example 1 of comparison, or 3 -- each -- the addition of aluminum -- this invention -- out of range -- further -- the examples 2 and 3 of comparison -- the addition of In -- this invention -- being out of range . For this reason, in the unleaded pewter of the example of comparison, a bond strength with sheet glass is low, and all pewter layers have exfoliated.

[0035] (Examples 15-24) Dissolution adhesion of the unleaded pewter which consists of composition shown in

Table 3 was carried out on the frequency of 60kHz on the sheet glass using the ultrasonic soldering iron with which the trowel point vibrates, using a soda lime glass (50x50x3mm) as jointed material, and the sample of this example was created. Each composition of front Naka is a weight % display.

[0036] The ablation degree of the unleaded pewter at the time of deleting with a knife the pewter layer pasted up on the sheet glass front face like the case of the aforementioned examples 1-14 performed adhesive evaluation of sheet glass and a pewter. As for the thing and x mark with which O mark remained on sheet glass in the adhesive column in Table 3, without more than the half of a pewter layer exfoliating, all pewter layers exfoliate.

[0037]

[Table 3]

	実施例15	実施例16	実施例17	実施例18	実施例19	実施例20	実施例21	実施例22	実施例23	実施例24
S n	56	72	66	59	55	64	68	57	64	67.5
A l	1	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
I n	28	18	28	30	40	28	28	38	28	28
A g	2	2	2.5	2.5	2.45	2.45	2.45	2.45	2	2
C u	0	0	0	0	0	0	0	0	0	0
Z n	5	2	1	3	2	5	1	1.55	5	2
S b	5	0	2	0	0	0	0	0	0	0
T I	3	0	0	0	0	0	0	0	0	0
S i	0	2	0	0	0	0	0	0	0	0
B i	0	3	0	5	0	0	0	0	0	0
F	0	0	0	0	0.05	0	0	0	0	0
N i	0	0	0	0	0	0.05	0	0	0	0
C	0	0	0	0	0	0	0.05	0	0	0
G a	0	0	0	0	0	0	0	0.5	0	0
G e	0	0	0	0	0	0	0	0	0.05	0
P	0	0	0	0	0	0	0	0	0	0.001
合計	100	100	100	100	100	100	100	100	100	100.001
接着性	O	O	O	O	O	O	O	O	O	O

[0038] So that clearly from Table 3 the sample of this example By adding appropriately a component and the minute amount addition component of Fe, nickel, Co, Ga, germanium, and P as shown in the claim 7 besides the component shown in a claim 1 Since it not only increases a bond strength with glass, but has various properties required in order to paste up firmly pewters, such as own mechanical strength of a pewter and distortion relief of the glass-pewter interface at the time of cooling, and glass, Glass can be firmly joined with a pewter and the problem of ablation by the shock after soldering etc. is not produced at all.

[0039]

[Effect of the Invention] As explained above, the unleaded pewter of this invention does not contain the lead of a toxic substance. By adding appropriately a component and the minute amount addition component of Fe, nickel, Co, Ga, germanium, and P as contained the component shown in a claim 1 and shown in a claim 7 Since it not only increases a bond strength with glass, but has various properties required in order to paste up firmly pewters, such as own mechanical strength of a pewter and distortion relief of the glass-pewter interface at the time of cooling, and oxide material, such as glass Oxide material, such as glass and ceramics, can be firmly joined with a pewter, and it has the outstanding effect of moreover being hard to produce ablation after soldering.

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] this invention relates to the unleaded pewter for oxide material junction of the ceramics which can work at low temperature, glass, etc.

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PRIOR ART

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[Description of the Prior Art] Although the method of performing electroplating and electroless deposition, such as gold plate, copper coating, and nickel plating, beforehand for soldering of oxide material, such as ceramics and glass, is common knowledge conventionally, to solder at an expensive price [ soldering to a plating side ], intricately, and more economically is demanded.

[0003] It is indicated by glass and ceramics about the Pb-Sn system pewter which can carry out direct soldering at JP,49-22299,B or JP,52-21980,B to meet this request.

[0004] However, lead is a strong toxic metal, we are anxious about the influence of the health and environment on leaden, the bad influence to an ecosystem and contamination are being regarded as questionable, and the movement which makes a pewter unleaded is spreading quickly in recent years.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] As explained above, the unleaded pewter of this invention does not contain the lead of a toxic substance. By adding appropriately a component and the minute amount addition component of Fe, nickel, Co, Ga, germanium, and P as contained the component shown in a claim 1 and shown in a claim 7 In order to paste up firmly pewters, such as own mechanical strength of a pewter and distortion relief of the glass-pewter interface at the time of cooling, and oxide material, such as glass, it not only to increase a bond strength with glass, but. Since it has required various properties, oxide material, such as glass and ceramics, can be firmly joined with a pewter, and it has the outstanding effect of moreover being hard to produce exfoliation after soldering.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Although the pewter currently indicated by above-mentioned JP,49-22299,B is a Pb-Sn-Cd-Sb pewter in which direct soldering to oxide film material, such as glass and ceramics, is possible, since this pewter contains the lead of a toxic substance, if the waste of the product using these pewters is exposed to acid rain, lead will be eluted in large quantities and the toxicity will pose a very serious problem.

[0006] Moreover, although the pewter indicated by above-mentioned JP,52-21980,B is a rare earth-metal content pewter usable to junction of oxide material, such as glass and ceramics, a principal component is lead and this pewter also has the same problem.

[0007] On the other hand, as a unleaded pewter, research is mainly briskly made as an object for electronic-parts mounting. For example, although it is indicated by JP,9-326554,A about the Sn-Ag-In pewter and indicated by JP,8-164495,A about the Sn-Zn-Bi pewter, all have the trouble that the bonding strength of a pewter is not enough, in soldering to oxide material, such as glass and ceramics.

[0008] Furthermore, although indicated by JP,55-36032,B about the Sn-Ag-aluminum-Zn pewter to the metallic oxide as a unleaded pewter which can be soldered, since the metal is chosen as a transconjugant, when it is used to oxide material which a coefficient of thermal expansion is large and is different, such as glass and ceramics, it has the trouble of being easy to exfoliate.

[0009] this invention is made in view of the above-mentioned conventional actual condition, and it aims at offering the unleaded pewter which has sufficient bonding strength to oxide material, such as glass and ceramics, excluding the lead of a toxic substance.

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## MEANS

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[Means for Solving the Problem] this invention is made in order to join oxides, such as glass and ceramics, and it is considered as the composition which contains aluminum, In, Ag, Cu, and Zn in the pewter which makes Sn a principal component.

[0011] That is, the unleaded pewter of this invention is displayed by weight %, and 0.01 - 3.0% of aluminum, 0.1 - 50% of In, 0.1 - 6.0% of Ag, 0 - 6.0% of Cu, 0 - 10.0% of Zn, and the remainder are characterized by the bird clapper from Sn.

[0012] Here, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.01 - 1.0% of aluminum.

[0013] Moreover, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.1 - 30% of In.

[0014] Furthermore, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.1 - 3.5% of Ag.

[0015] Furthermore, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.1 - 1.0% of Cu.

[0016] Furthermore, as for the unleaded pewter of this invention, it is desirable as the component to contain 0.01 - 7.0% of Zn.

[0017] Moreover, as for the unleaded pewter of this invention, it is desirable to contain one or more kinds of elements chosen from among Sb, Ti, Si, or Bi in a total of 10% or less of range.

[0018] Below, the reason for composition limitation of the unleaded pewter of this invention is explained. However, the following composition is displayed by weight %.

[0019] Since Sn has operation of there being no toxicity and obtaining wetting to a transconjugant, it is a component indispensable to a pewter.

[0020] Although aluminum is an element which is very easy to oxidize, it has the advantage of being easy to build combination in junction to an oxide. At less than 0.01%, the effect has low aluminum addition, when it exceeds 3.0%, while it is difficult for own hardness of a pewter to secure increase and thermo-cycle-proof nature, the melting point is high, and workability gets worse. A more desirable addition is 0.01 - 1.0% of range.

[0021] It raises wettability and it not only reduces the melting point of a pewter, but it has operation of making the pewter itself soft. If In addition is low and the effect exceeds 50% at less than 0.1%, it will become a pewter's own on-the-strength securing not only becoming difficult but quite [ in cost ] expensive conversely. The range of a more desirable addition is 0.1 - 30%.

[0022] Ag demonstrates the effect excellent in improvement in the mechanical strength of a pewter by adding. At less than 0.1%, the effect has low Ag addition, improvement in a mechanical strength is not obtained, but if it exceeds 6.0%, while the melting point will become high, an intermetallic compound with Sn occurs so much, and that a mechanical strength falls conversely poses a problem. The range of a more desirable addition is 0.1 - 3.5%.

[0023] Cu demonstrates the effect which was excellent in improvement in the mechanical strength of a pewter by adding like above-mentioned Ag. If Cu addition exceeds 6.0%, while the melting point will become high like Ag, an intermetallic compound with Sn occurs so much, and that a mechanical strength falls conversely poses a problem. The range of a more desirable addition is 0.1 - 1.0%.

[0024] Zn is added by the pewter in order to give the adhesive strength to oxide material, such as glass and

ceramics. If Zn addition exceeds 10.0%, the inclination for a pewter to become weak becomes remarkable and it is not desirable practically. The range of a more desirable addition is 0.01 - 7.0%, and the still more desirable range is 0.5 - 5.0%.

[0025] In the unleaded pewter of this invention, one or more kinds of elements can be suitably added in 10% or less of range among Sb, Ti, Si, or Bi. Sb makes soldering appearance good and increases creep resistance. Ti, Si, and Bi can make the wettability of a pewter improve. moreover -- in addition -- even if it carries out minute amount addition of the elements, such as Fe, nickel, Co, Ga, germanium, and P, -- the property as a pewter --

[0026] In addition, the unleaded pewter of this invention can be soldered direct to the difficulty soldering metal which has oxide skins, such as aluminum besides oxide material, such as glass and ceramics, titanium, and a zirconium. Moreover, when soldering to difficulty soldering material, it is desirable to use the equipment which can add supersonic oscillation to a pewter in the case of soldering.

[0027]

[Embodiments of the Invention] Hereafter, a concrete example is given and the operation form of this invention is explained.

[0028] (Examples 1-14) Dissolution adhesion of the unleaded pewter which consists of composition shown in Tables 1 and 2 was carried out on the frequency of 60kHz on the sheet glass using the ultrasonic soldering iron with which the trowel point vibrates, using a soda lime glass (50x50x3mm) as jointed material, and the sample of this example was created. Each composition of front Naka is a weight % display.

[0029] The exfoliation degree of the unleaded pewter at the time of deleting with a knife the unleaded pewter layer pasted up on the sheet glass front face performed adhesive evaluation of sheet glass and a unleaded pewter. As for the thing and x mark with which O mark remained on sheet glass in the adhesive column in Table 1 and 2, without more than the half of a pewter layer exfoliating, all pewter layers exfoliate.

[0030]

[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10
S n	62.2	63.95	45.5	88	85	70.5	50	67	76	65
A l	0.5	0.05	2.5	0.5	0.5	1	2.5	0.5	0.5	1
I n	30	28	40	1	10	26	45	30	15	28
A g	2.3	2.5	2.5	3.5	3	2	1.5	0.5	6	2.3
C u	0	0	0	0	0	0	0	0	0.5	0.7
Z n	5	5.5	9.5	7	1.5	0.5	1	2	2	3
合計	100	100	100	100	100	100	100	100	100	100
接着性	○	○	○	○	○	○	○	○	○	○

[0031]

[Table 2]

	実施例11	実施例12	実施例13	実施例14	比較例 1	比較例 2	比較例 3
S n	65	69	64	68	77.2	70	96.5
A l	0.5	0.5	1	0.95	0	0	0
I n	26	26	28	28.4	20	0	0
A g	2.5	0.5	2	2.5	2.8	0	3.5
C u	5	3	2	0.05	0	1	0
Z n	1	1	3	0.1	0	29	0
合計	100	100	100	100	100	100	100
接着性	○	○	○	○	×	×	×

[0032] So that clearly from Tables 1 and 2 the sample of this example By making components, such as aluminum, In, Zn, Ag, and Cu, contain appropriately, as shown in a claim 1 Since it not only increases a bond strength with glass, but has various properties required in order to paste up firmly pewters, such as own mechanical strength of a pewter and distortion relief of the glass-pewter interface at the time of cooling, and glass, Glass can be firmly joined with a pewter and the problem of exfoliation by the shock after soldering etc. is not produced at all.

[0033] (The example 1 of comparison, or 3) The composition and the adhesive property of the example of comparison over this invention are shown in Table 2. Composition is a weight % display.

[0034] the example 1 of comparison, or 3 -- each -- the addition of aluminum -- this invention -- out of range -- further -- the examples 2 and 3 of comparison -- the addition of In -- this invention -- being out of range . For this reason, in the unleaded pewter of the example of comparison, a bond strength with sheet glass is low, and all pewter layers have exfoliated.

[0035] (Examples 15-24) Dissolution adhesion of the unleaded pewter which consists of composition shown in Table 3 was carried out on the frequency of 60kHz on the sheet glass using the ultrasonic soldering iron with which the trowel point vibrates, using a soda lime glass (50x50x3mm) as jointed material, and the sample of this example was created. Each composition of front Naka is a weight % display.

[0036] The exfoliation degree of the unleaded pewter at the time of deleting with a knife the pewter layer pasted up on the sheet glass front face like the case of the aforementioned examples 1-14 performed adhesive evaluation of sheet glass and a pewter. As for the thing and x mark with which O mark remained on sheet glass in the adhesive column in Table 3, without more than the half of a pewter layer exfoliating, all pewter layers exfoliate.

[0037]

[Table 3]

	実施例15	実施例16	実施例17	実施例18	実施例19	実施例20	実施例21	実施例22	実施例23	実施例24
S n	56	72	66	59	55	64	68	57	64	67.5
A l	1	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
I n	28	18	28	30	40	28	28	38	28	28
A g	2	2	2.5	2.5	2.45	2.45	2.45	2.45	2	2
C u	0	0	0	0	0	0	0	0	0	0
Z n	5	2	1	3	2	5	1	1.55	5	2
S b	5	0	2	0	0	0	0	0	0	0
T I	3	0	0	0	0	0	0	0	0	0
S I	0	2	0	0	0	0	0	0	0	0
B i	0	3	0	5	0	0	0	0	0	0
F e	0	0	0	0	0.05	0	0	0	0	0
N i	0	0	0	0	0	0.05	0	0	0	0
C	0	0	0	0	0	0	0.05	0	0	0
G a	0	0	0	0	0	0	0	0.5	0	0
G e	0	0	0	0	0	0	0	0	0.05	0
P	0	0	0	0	0	0	0	0	0	0.001
合計	100	100	100	100	100	100	100	100	100	100.001
接着性	○	○	○	○	○	○	○	○	○	○

[0038] So that clearly from Table 3 the sample of this example By adding appropriately a component and the minute amount addition component of Fe, nickel, Co, Ga, germanium, and P as shown in the claim 7 besides the component shown in a claim 1 Since it not only increases a bond strength with glass, but has various properties required in order to paste up firmly pewters, such as own mechanical strength of a pewter and distortion relief of the glass-pewter interface at the time of cooling, and glass, Glass can be firmly joined with a pewter and the problem of exfoliation by the shock after soldering etc. is not produced at all.

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[Translation done.]

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